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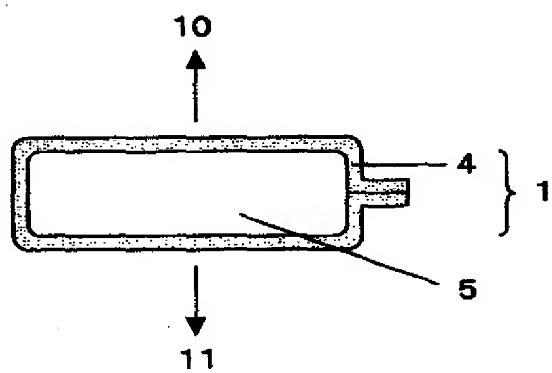
最終頁に続く

(54)【発明の名称】 真空断熱材

(57)【要約】

【課題】 本発明は、真空断熱材の外装体を通しての熱の移動がなく十分な断熱性能が得られ、且つ、外装体のガスバリア性が高く、長期に亘って外装体内部の真空状態が保たれ、断熱性能が維持される真空断熱材を提供することにある。

【解決手段】 ガスバリア性を有する積層フィルムからなる外装体内部に断熱コア材を封入し、その外装体内部を真空排気した真空断熱材において、前記積層フィルムが、支持基材上に形成された有機物膜と無機物膜との積層膜を含むことを特徴とする真空断熱材を提供する。



1

【特許請求の範囲】

【請求項１】ガスバリア性を有する積層フィルムからなる外装体内部に断熱コア材を封入し、その外装体内部を真空排気した真空断熱材において、前記積層フィルムが、支持基材上に形成された有機物膜と無機物膜との積層膜を含むことを特徴とする真空断熱材。

【請求項２】前記有機物膜が、電子線または紫外線重合性樹脂を、電子線または紫外線によって重合硬化させたものであることを特徴とする請求項１に記載の真空断熱材。

【請求項３】前記無機物膜の厚さが、５ｎｍ以上５００ｎｍ以下であることを特徴とする請求項１または２に記載の真空断熱材。

【請求項４】ガスバリア性を有する２枚の積層フィルムからなる外装体内部に断熱コア材を封入し、その外装体内部を真空排気した真空断熱材において、前記積層フィルムのうち少なくとも１枚が、支持基材上に形成された有機物膜と無機物膜との積層膜を含むことを特徴とする真空断熱材。

【請求項５】前記積層フィルムのうち、高温側に位置する１枚が、熱反射性の材料を含むことを特徴とする請求項４のいずれかに記載の真空断熱材。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、冷蔵庫や低温コンテナ等に取り付けて、断熱効果を発揮する真空断熱材に関するものである。

【０００２】

【従来の技術】冷蔵庫や低温コンテナ等には、従来から種々の断熱材が用いられており、特に、断熱性能の優れた断熱材として、断熱性のコア材を外装体内に封入し、内部を真空排気した構成の真空断熱材が使用されている。この外装体は、外部からのガス（空気）の侵入を防ぎ、内部を長期間真空状態に保持するために、ガスバリア性に優れたものである必要がある。そこで、従来、高いガスバリア性を持たすために、外装体のガスバリア層のとして７〜１５μｍ程度の厚さの金属アルミニウム箔を含む積層フィルムが主として用いられてきた。

【０００３】

【発明が解決しようとする課題】しかし、このようなアルミ箔の場合、ガスバリア性には優れているが、アルミニウム自体の熱伝導率が高いため、外装体を通しての熱伝導〔ヒートブリッジ〕によって、十分な断熱性能が得られないという問題があった。この問題の解決を目的として、外装体のガスバリア層に、熱伝導率が比較的小さいステンレス箔などを用いる方法〔特開平８−１５９３７６号公報〕やアルミニウムの蒸着膜を用いる方法、セラミックスやガラスの蒸着膜を用いる方法〔特開平７−１１３４９３号公報、特開平８−１５２２５８号公報〕などが発明されている。

2

【０００４】しかし、ステンレス箔などを用いる方法では、まだなおステンレスの熱伝導率が高いためにヒートブリッジの低減が不十分である。また、アルミニウムやセラミックスあるいはガラスの蒸着膜を用いる方法では、ヒートブリッジの低減は十分であるが、蒸着膜にピンホールやクラックが存在するためガスバリア性が不十分であり、長期間に亘って、外装体の内部を真空状態に保っておくことが不可能であった。本発明はこのような事情に鑑みてなされたもので、その目的とするところは、真空断熱材の外装体を通しての熱の移動がなく十分な断熱性能が得られ、且つ、外装体のガスバリア性が高く、長期に亘って外装体内部の真空状態が保たれ、断熱性能が維持される真空断熱材を提供することである。

【０００５】

【発明を解決するための手段】請求項１に記載の発明は、ガスバリア性を有する積層フィルムからなる外装体内部に断熱コア材を封入し、その外装体内部を真空排気した真空断熱材において、前記積層フィルムが、支持基材上に形成された有機物膜と無機物膜との積層膜を含むことを特徴とする真空断熱材である。

【０００６】請求項２に記載の発明は、前記有機物膜が、電子線または紫外線重合性樹脂を、電子線または紫外線によって重合硬化させたものであることを特徴とする請求項１に記載の真空断熱材である。

【０００７】請求項３に記載の発明は、前記無機物膜の厚さが、５ｎｍ以上５００ｎｍ以下であることを特徴とする請求項１または２に記載の真空断熱材である。

【０００８】請求項４に記載の発明は、ガスバリア性を有する２枚の積層フィルムからなる外装体内部に断熱コア材を封入し、その外装体内部を真空排気した真空断熱材において、前記積層フィルムのうち少なくとも１枚が、支持基材上に形成された有機物膜と無機物膜との積層膜を含むことを特徴とする真空断熱材である。

【０００９】請求項５に記載の発明は、前記積層フィルムのうち、高温側に位置する１枚が、熱反射性の材料を含むことを特徴とする請求項４のいずれかに記載の真空断熱材である。

【００１０】

【発明の実施の形態】以下、本発明の一実施の形態を図を用いて詳細に説明する。本発明の真空断熱材は、ガスバリア性を有する積層フィルムを含む外装体１の内部に断熱コア材５が封入され、外装体内部が真空排気されているものであって、前記積層フィルム、有機物膜７と無機物膜８との積層膜を含むことを特徴とするものである。本発明の真空断熱材は、ガスバリア性を有する積層フィルム２、３をからなる外装体からなり、最後に４方シールして真空断熱材としてもよいし（図１）、１枚のガスバリア性を有する積層フィルム４をからなる外装体からなり、最後に３方シールして真空断熱材としてもよい（図２）。

【００１１】本発明の有機物膜と無機物膜との積層膜を含む積層フィルムは、少なくとも支持基材上に有機物膜と無機物膜との積層膜を形成したものである。支持基材としては、ポリエチレンテレフタレート（ＰＥＴ）、ポリエチレンナフタレート（ＰＥＮ）、ポリブチレンテレフタレート（ＰＢＴ）などのポリエステル、ポリエチレン（ＰＥ）、ポリプロピレン（ＰＰ）、ポリスチレン（ＰＳ）などのポリオレフィン、ナイロン－６、ナイロン－６６などのポリアミド（ＰＡ）、ポリイミド、ポリアクリレート、ポリ塩化ビニル（ＰＶＣ）、ポリ塩化ビニリデン（ＰＶＤＣ）、ポリビニルアルコール（ＰＶＡ）、エチレン－ビニルアルコール共重合体（ＥＶＯＨ）、ポリカーボネート（ＰＣ）、ポリエーテルスルフォン（ＰＥＳ）、ポリメチルメタクリレート（ＰＭＭＡ）などやこれらの共重合体の無延伸あるいは延伸フィルムである。これらの支持基材の表面は、有機物膜と無機物膜との積層膜の形成に先立って、コロナ処理、火炎処理、低温プラズマ処理、薬品処理等の表面処理が施されていても差し支えない。またこれらのプラスチックフィルムには、必要に応じて帯電防止剤や紫外線吸収剤、可塑剤、滑剤などといった添加剤が含まれていても構わない。

【００１２】本発明における無機物膜としては、金属アルミニウム（Ａｌ）、酸化アルミニウム（ＡｌＯｘ）、酸化珪素（ＳｉＯｘ）、酸化マグネシウム（ＭｇＯ）、酸化カルシウム（ＣａＯ）、酸化チタン（TiO_2）、酸化ジルコニウム（ZrO_2）、窒化アルミニウム（ＡｌＮ）、窒化チタン（ＴｉＮ）、窒化珪素（Si_3N_4）、酸窒化アルミニウム（ＡｌＯｘＮｙ）、酸窒化珪素（ＳｉＯｘＮｙ）、酸窒化チタン（ＴｉＯｘＮｙ）、インジウム錫酸化物（ＩＴＯ）、インジウムセリウム酸化物（ＩＣＯ）などの無機物の単独膜もしくは複数の無機物の混合物膜や積層膜が用いられる。このような無機物膜は、真空蒸着法、スパッタリング法、化学的蒸着法（ＣＶＤ法）などの真空プロセスによって形成される。また、その厚さは無機物膜の種類によって若干異なるが、５ｎｍ以上、５００ｎｍ以下であることが重要である。５ｎｍ以下であると支持基材上に設けられた無機物が島状になって膜状にならない場合があり、５００ｎｍ以上の場合には、膜自身の内部応力によって、膜が割れたり、支持基材から剥がれたりする場合があるためである。また、無機物膜がＡｌの場合には、ヒートブリッジが大きくなって、断熱性能が低下することがあるため、特に５００ｎｍ以下であることが重要である。また、ガスバリア性能や断熱性能を阻害しない程度であれば、このような無機物膜中にその他の成分が含まれていても差し支えない。

【００１３】本発明における有機物膜は、支持基材表面の凹凸を平滑にすること、無機物膜のクラックや欠陥の伝播を遮断すること、無機物膜中の内部応力を緩和すること、無機物膜を保護すること、などを目的として設けられるもので、これらの目的に添うものであれば、その成分や組成、厚さ、形成方法など、いずれも特に限定されるものではない。しかし、重合硬化速度の速さや塗工後のエージングが不要であることなどから紫外線あるいは電子線重合性の樹脂を、紫外線あるいは電子線で硬化させたものであることが好ましい。

【００１４】具体的には、イソアミルアクリレート、ラウリルアクリレート、ステアリルアクリレート、ブトキシエチルアクリレート、エトキシジエチレングリコールアクリレート、メトキシトリエチレングリコールアクリレート、メトキシポリエチレングリコールアクリレート、メトキシジプロピレングリコールアクリレート、フェノキシエチルアクリレート、フェノキシポリエチレングリコールアクリレート、フェノールＥＯ変性アクリレート、ノニルフェノールＥＯ変性アクリレート、テトラヒドロフルフリルアクリレート、イソボニルアクリレート、２－ヒドロキシエチルアクリレート、２－ヒドロキシプロピルアクリレート、２－ヒドロキシ－３－フェノキシプロピルアクリレート、２－アクリロイロキシエチルコハク酸、２－アクリロイロキシエチルフタル酸、２－アクリロイロキシエチル－２－ヒドロキシエチルフタル酸、２－エチルヘキシルカルビトールアクリレート、Ｎ－ビニル－２－ピロリドンなどの単官能アクリレート、メチルメタクリレート、エチルメタクリレート、ｎ－ブチルメタクリレート、イソブチルメタクリレート、２－エチルヘキシルメタクリレート、イソデシルメタクリレート、ｎ－ラウリルメタクリレート、アルキルメタクリレート、トリデシルメタクリレート、ｎ－ステアリルメタクリレート、メトキシエチレングリコールメタクリレート、メトキシポリエチレングリコールメタクリレート、シクロヘキシルメタクリレート、テトラヒドロフルフリルメタクリレート、ベンジルメタクリレート、フェノキシエチルメタクリレート、イソボニルメタクリレート、２－ヒドロキシエチルメタクリレート、２－ヒドロキシプロピルメタクリレート、２－ヒドロキシブチルメタクリレート、ジメチルアミノエチルメタクリレート、ジエチルアミノエチルメタクリレート、メタクリル酸、２－メタクリロイロキシエチルコハク酸、２－メタクリロイロキシエチルヘキサヒドロフタル酸、２－メタクリロイロキシエチル－２－ヒドロキシプロピルフタレート、グリシジルメタクリレートなどの単官能メタクリレート、トリエチレングリコールジアクリレート、ポリエチレングリコールジアクリレート、ネオペンチルグリコールジアクリレート、１．６－ヘキサンジオールジアクリレート、１．９－ノナンジオールジアクリレート、ジメチロールトリシクロデカンジアクリレート、エチレングリコールジメタクリレート、ジエチレングリコールジメタクリレート、１．４－ブタンジオールジメタクリレート、１．６－ヘキサンジオールジメタクリレート、

１，９－ノナンジオールジメタクリレート、グリセリンジメタクリレート、２－ヒドロキシ－３－アクリロイロキシプロピルメタクリレートなどの２官能のアクリレートやメタクリレート、トリメチロールプロパントリアクリレート、ペンタエリスリトールトリアクリレート、ペンタエリスリトールテトラアクリレート、ジペンタエリスリトールヘキサアクリレート、トリメチロールプロパントリメタクリレート、ペンタエリスリトールトリアクリレートヘキサメチレンジイソシアネート、ペンタエリスリトールトリアクリレートトリレンジイソシアネート、ペンタエリスリトールトリアクリレートイソホロンジイソシアネート、ジペンタエリスリトールヘキサアクリレート、ジペンタエリスリトールヘキサアクリレートカプロラクトン付加物、ソルビトールヘキサアクリレートエチレンオキサイド（ＥＯ）付加物などの３官能以上のアクリレートやメタクリレート、などが挙げられるがこれらに限定されるものではない。

【００１５】また、これらのアクリレートやメタクリレートを単独で用いても良いし、２つ以上を混ぜ合わせて用いても良い。特に、単官能のアクリレートやメタクリレートの場合は、２官能以上のアクリレートやメタクリレートと混合して用いられる。また、その他の紫外線硬化性や電子線硬化性を持たない有機化合物と混ぜ合わせて用いても良い。

【００１６】このような有機物膜は、紫外線や電子線を照射することによって重合硬化するため、成膜速度が速い、エージングなどの後処理を必要としない、真空中での成膜も可能であり、不純物の混入が避けられる上に、無機物を成膜するための真空プロセスとのインライン化が可能である、などの優れた特徴を持っているものである。　また、その厚さは有機物の種類やコーティング方法、硬化手段などによって異なるが、概ね０．２～５．０μｍ程度が好適である。０．２μｍよりも薄いと有機物膜が連続膜にならない場合があるためであり、５．０μｍよりも厚いと、有機物膜の硬化収縮によって無機物膜にストレスがかかり、バリア性の低下が見られる場合があるためである。

【００１７】このような有機物膜の成膜方法としては、所望の有機物やその混合物を溶剤に溶かしてグラビアコーティングなどの方法でコーティングした後、オーブンなどで溶剤を揮発させ、次いで紫外線や電子線を照射して重合硬化させるのも一つの方法である。また、所望の有機物やその混合物を真空中で蒸発させ、冷却した基材上に液体膜として凝縮させた後、紫外線や電子線を照射して重合硬化させてもよく、この場合、真空中での蒸発方法としては、フラッシュ蒸発法が、所望の組成の有機物膜が容易に、しかも高速で得られることから、最も適した方法であると言える。

【００１８】また、前記有機物膜と無機物膜との積層順序や層数には特に制限はなく、複数の有機物膜や無機物膜が同一のものであっても良いし、別のものであってもよい。また、有機物膜と無機物膜の他にさらに他の機能層を積層して積層フィルムとしてもよい。例えば、突き刺し強度を向上させるためにナイロン等を積層することができる。

【００１９】本発明では、前記外装体構成するガスバリア性を有する積層フィルムが２枚であってもよく、その場合、高温側の積層フィルムが、熱反射性の材料を含んでいることが好ましく、低温側の積層フィルムが、前記有機物膜と無機物膜との積層膜を含んでいることが好ましい。熱反射材料としては、例えば金属箔などが挙げられる。このようにすれば高温側からの熱を反射し、低温側への熱の伝導を低減することができる。

【００２０】さらに積層フィルム２、３、４は、最外層にポリエチレン、ポリプロピレン、エチレン共重合体等ヒートシール性を有する樹脂からなるシーラント層９が積層されてなるものである。このようなシーラント層は、フィルム化した材料を接着剤（図示せず）を介してラミネートしたり、溶融した樹脂を直接押出すことによって積層される。

【００２１】また、本発明の真空断熱材として用いるためには前記積層フィルム２，３，４のガスバリア性として、酸素透過度、水蒸気透過度がそれぞれ０．５（cm^3/m^2・ｄａｙ）、０．１（g/m^2・ｄａｙ）以下であると好ましく、０．１（cm^3/m^2・ｄａｙ）、０．０５（g/m^2・ｄａｙ）以下であるとさらに好ましい。

【００２２】このような構成からなる積層体のヒートシール性樹脂層を内面として、断熱性コア材４を充填し真空包装することによって本発明の真空断熱材を得ることが出来る。この断熱性コア材料は、シリカやパーライト、ケイ酸カルシウム等の粉末を一定の形状に成形した成形体等が使用される。

【００２３】

【実施例】次に、本発明の真空断熱材を具体的な一実施例を挙げて、さらに詳しく説明する。

【００２４】<実施例１>厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体５とし、その片面に乾燥後の厚さが約１μｍになるようにアクリレートモノマー〔トリエチレングリコールジアクリレート〕（以下Ａｃ１）をコーティングし、加速電圧１２０ｋＶ、照射線量１０Ｍｒａｄの電子線を照射して硬化させることによって有機物膜７を形成した。続いてこの有機物膜７上に電子線加熱式巻取り蒸着装置を用いて厚さ約４０ｎｍの酸化珪素（以下ＳｉＯｘ）を成膜し無機物膜８とした後、無機物膜８上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層９とし、本発明の積層フィルム４を得た。次いで、この積層フィルムのシーラント層９同士を向かい合わせ、周辺をヒー

トシールし、断熱コア材５として粉末シリカの成形体を真空密封し、図１に示す真空断熱材を得た。この真空断熱材の外装体のガスバリア性〔酸素透過速度、水蒸気透過速度〕およびこの真空断熱材中央部で測定した熱伝導率を表１に示した。

【００２５】＜実施例２＞有機物膜、無機物膜を実施例１と同様の厚さ、方法で支持体側から順にＡｃ１／ＳｉＯｘ／Ａｃ１／ＳｉＯｘ／Ａｃ１のように設けた以外は、実施例１と同様の方法で、本発明の積層フィルム４を得た。この積層フィルムのシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００２６】＜実施例３＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体５とし、その片面に乾燥後の厚さが約１μｍになるように５重量％の光重合開始剤〔イルガキュア１８４　チバ・スペシャルティ・ケミカルズ製〕を含むアクリレートモノマー〔トリプロピレングリコールジアクリレート〕（以下Ａｃ２）をコーティングし、１２０ｍＪ／ｃｍ^{2}の紫外線を照射して硬化させることによって有機物膜７を形成した。続いてこの有機物膜７上に、無機物膜８として電子線加熱式巻取り蒸着装置を用いて厚さ約４０ｎｍの金属アルミニウム（以下Ａｌ）を成膜した後、金属アルミニウム膜上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層９とし、本発明の積層フィルム４を得た。この積層フィルムのシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００２７】＜実施例４＞有機物膜、無機物膜を実施例３と同様の厚さ、方法で支持体側から順にＡｃ２／Ａｌ／Ａｃ２／Ａｌ／Ａｃ２のように設けた以外は、実施例３と同様の方法で、本発明の積層フィルム４を得た。この積層フィルムのシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００２８】＜実施例５＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体５とし、その片面に乾燥後の厚さが約１μｍになるようにアクリレートモノマー〔ペンタエリスリトールトリアクリレートヘキサメチレンジイソシアネート〕（以下Ａｃ３）をコーティングし、加速電圧１２０ｋＶ、照射線量１０Ｍｒａｄの電子線を照射して硬化させることによって有機物膜７を形成した。続いてこの有機物膜７上に、無機物膜８として直流マグネトロン式巻取りスパッタリング装置を用いて厚さ約５０ｎｍのインジウムセリウム酸化物（以下ＩＣＯ）を成膜した後、この酸化物膜上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層９とし、本発明の積層フィルム４を得た。この積層フィルムのシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００２９】＜実施例６＞有機物膜、無機物膜を実施例５と同様の厚さ、方法で支持体側から順にＡｃ３／ＩＣＯ／Ａｃ３／ＩＣＯ／Ａｃ３のように設けた以外は、実施例５と同様の方法で、本発明の積層フィルム４を得た。この積層フィルムのシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３０】＜実施例７＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、実施例３と同様の方法で、厚さ約４０ｎｍの金属アルミニウム（Ａｌ）の蒸着層を設け、その上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし高温側の積層フィルム２を得た。有機物膜、無機物膜を実施例１と同様の厚さ、方法で支持体側から順にＡｃ１／ＳｉＯｘ／Ａｃ１／ＳｉＯｘ／Ａｃ１のように設けた以外は、実施例１と同様の方法で、本発明の低温側の積層フィルム３を得た次いで、この積層フィルム２、３のシーラント層９同士を向かい合わせ、周辺をヒートシールし、断熱コア材５として粉末シリカの成形体を真空密封し、図２に示す真空断熱材を得た。この真空断熱材の外装体のガスバリア性〔酸素透過速度、水蒸気透過速度〕およびこの真空断熱材中央部で測定した熱伝導率を表１に示した。

【００３１】＜比較例１＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、実施例１と同様の方法で、厚さ約４０ｎｍの酸化珪素層（ＳｉＯｘ）を設け、その上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし、積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３２】＜比較例２＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、実施例３と同様の方法で、厚さ約４０ｎｍの金属アルミニウム（Ａｌ）の蒸着層を設け、その上にポリエス

テルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３３】＜比較例３＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、実施例５と同様の方法で、約５０ｎｍのインジウムセリウム酸化物層（ＩＣＯ）を設け、その上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし、積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３４】＜比較例４＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、乾燥後の厚さが約１μｍになるようにアクリレートモノマー〔トリエチレングリコールジアクリレート〕（Ａｃ１）をコーティングし、加速電圧１２０ｋＶ、照射線量１０Ｍｒａｄの電子線を照射して硬化させることによってポリマー層を形成した。そのアクリレート層上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし、積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３５】＜比較例５＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、乾燥後の厚さが約１μｍになるように５重量％の光重合開始剤〔イルガキュア１８４　チバ・スペシャルティ・ケミカルズ製〕を含むアクリレートモノマー〔トリプロピレングリコールジアクリレート〕（Ａｃ２）をコ＊ーティングし、１２０ｍＪ／ｃｍ²の紫外線を照射して硬化させることによってポリマー層を形成した。続いてこのアクリレート層上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし、積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３６】＜比較例６＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、乾燥後の厚さが約１μｍになるようにアクリレートモノマー〔ペンタエリスリトールトリアクリレートヘキサメチレンジイソシアネート〕（Ａｃ３）をコーティングし、加速電圧１２０ｋＶ、照射線量１０Ｍｒａｄの電子線を照射して硬化させることによってポリマー層を形成した。続いてこのアクリレート層上にポリエステルウレタン系接着剤（図示せず）を介して厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし、積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３７】＜比較例７＞厚さ１２μｍのＰＥＴフィルム〔ルミラーＰ６０　東レ製〕を支持体とし、その片面に、ポリエステルウレタン系接着剤（図示せず）を介して厚さ７μｍの金属アルミニウム箔をラミネートし、続いてこの金属アルミニウム箔上に、同じ接着剤を用いて厚さ６０μｍの低密度ポリエチレンフィルムをラミネートしてシーラント層とし、積層体を得た。この積層体のシーラント層同士を向かい合わせ、周辺をヒートシールし、粉末シリカの成形体を真空密封して得た真空断熱材のガスバリア性と熱伝導率を実施例１と同様にして測定した。その測定結果を表１に示した。

【００３８】

【表１】

	外装体中の積層フィルムの有機物膜、無機物膜の層構成	ガスバリア性		熱伝導率 (W/m·K)
		酸素 (cm³/m²·day)	水蒸気 (g/m²·day)	
実施例1	Ac1／SiOx	0.5	0.07	0.005
実施例2	Ac 1／SiOx／Ac 1／SiOx／Ac 1	0.02	0.02	0.005
実施例3	Ac 2／Al	0.05	0.05	0.006
実施例4	Ac 2／Al／Ac 2／Al／Ac 2	≦0.01	≦0.01	0.006
実施例5	Ac 3／ICO	≦0.01	≦0.01	0.005
実施例6	Ac 3／ICO／Ac 3／ICO／Ac 3	≦0.01	≦0.01	0.005
実施例7	高温側:Al 低温側:Ac 1／SiOx／Ac 1／SiOx／Ac 1	0.5	0.6	0.005
比較例1	SiOx	2.5	2	0.070
比較例2	Al	0.5	0.6	0.050
比較例3	ICO	2	2	0.050
比較例4	Ac 1	140	52	0.080
比較例5	Ac 2	140	52	0.080
比較例6	Ac 3	140	52	0.080
比較例7	Al箔	≦0.1	≦0.05	0.010

【００３９】実施例１～７に示したように、真空断熱材の外装体として、支持基材上に有機物膜と無機物膜との

積層膜を含むガスバリア性を有する積層フィルムを用いることにより、真空断熱材の内部を長期間に亘って高い真空度に保つために不可欠な高いガスバリア性を有する外装体が得られ、またヒートブリッジによる熱伝導が無く、高い断熱性能を有する真空断熱材が得られた。また、比較例１～３および比較例４～６に示した結果は、それぞれ無機物膜および有機物膜のみを積層フィルムとして用いた場合のものであるが、これらの外装体では実施例の場合ほどの高いガスバリア性が得られなかった。特に比較例４～６の場合では、有機物膜がガスバリア性の向上にほとんど寄与していないため、真空断熱材内部の真空度が始めから低く、他と比較して初期の熱伝導率も高かった。また、比較例７に示した結果は、金属アルミニウム箔をガスバリア性として用いた場合のものであるが、この外装体では実施例のものと比較しても十分なガスバリア性が得られたが、この外装体を用いた真空断熱材では、ヒートブリッジによる熱伝導によって、高い断熱性能が得られなかった。

【００４０】

【発明の効果】以上述べたように、本発明によれば、ガスバリア性を有する積層フィルムからなる外装体内に断熱コア材が封入され、その外装体内部が真空排気された真空断熱材において、前記積層フィルムが、支持基材上に形成された有機物膜と無機物膜との積層膜を含むこと＊によって、真空断熱材の外装体を通しての熱の移動がなく十分な断熱性能が得られ、且つ、外装体のガスバリア性が高く、長期に亘って外装体内部の真空状態が保たれ、断熱性能が維持される真空断熱材を提供することが出来る。

【００４１】

【図面の簡単な説明】

【図１】本発明の真空断熱材を示す断面図である。

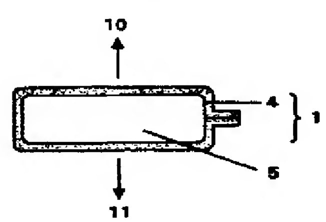
【図２】本発明の真空断熱材を示す断面図である。

【図３】本発明の真空断熱材の外装体を構成する積層フィルムの一例を示す断面図である。

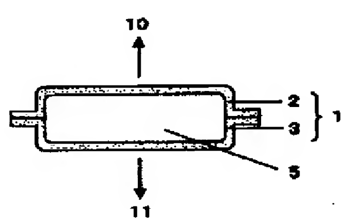
【符号の説明】

１　外装体
２　高温側の積層フィルム
３　低温側の積層フィルム
４　積層フィルム
５　断熱コア材
６　支持体
７　有機物膜
８　無機物膜
９　シーラント層
１０　高温側
１１　低温側

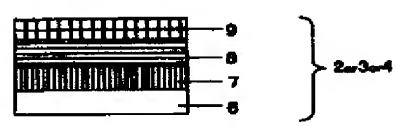
【図１】



【図２】



【図３】



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CA04 CA18 CA21 CA24 FB11
GA01 GA11 GA13
3H036 AA08 AA09 AB28 AC01 AE02
3L102 JA01 JA06 MB24
4F100 AA00D AA20 AH00C AK01A
AK01C AK01E AK06 AK25
AK42 AS00B BA04 BA05
BA07 DD31 DE01 EJ08C
GB90 JD02A JD02E JD07C
JD09C JJ02 JJ02B YY00D

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CLAIMS

[Claim(s)]
[Claim 1] Vacuum insulation material characterized by said laminated film containing the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material in the vacuum insulation material which enclosed heat insulation core material with the interior of the sheathing object which consists of a laminated film which has gas barrier property, and carried out evacuation of the interior of a sheathing object.
[Claim 2] Vacuum insulation material according to claim 1 to which said organic substance film is characterized by carrying out polymerization hardening of an electron ray or the ultraviolet-rays polymerization nature resin by the electron ray or ultraviolet rays.
[Claim 3] Vacuum insulation material according to claim 1 or 2 to which thickness of said inorganic substance film is characterized by 5nm or more being 500nm or less.
[Claim 4] Vacuum insulation material characterized by at least one in said laminated film containing the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material in the vacuum insulation material which enclosed heat insulation core material with the interior of the sheathing object which consists of a laminated film of two sheets which has gas barrier property, and carried out evacuation of the interior of a sheathing object.
[Claim 5] Vacuum insulation material given in either of claims 4 to which one sheet located in an elevated-temperature side among said laminated films is characterized by including the ingredient of thermal reflection.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is attached in a refrigerator, a low-temperature container, etc., and relates to the vacuum insulation material which demonstrates adiabatic efficiency.
[0002]
[Description of the Prior Art] Various heat insulators are used from the former, as a heat insulator which was excellent in heat insulation property especially, adiathermic core material is enclosed with the sheathing inside of the body, and the vacuum insulation material of a configuration of having carried out evacuation of the interior is used for the refrigerator or the low-temperature container. This sheathing object needs to be excellent in gas barrier property, in order to prevent invasion of the gas (air) from the outside and to hold the interior to a vacua for a long period of time. Then, in order to give high gas barrier property conventionally, the laminated film which contains metal aluminium foil with a thickness of about 7-15 micrometers as that of the gas barrier layer of a sheathing object has mainly been used.
[0003]
[Problem(s) to be Solved by the Invention] However, in the case of such aluminum foil, it excelled in gas barrier property, but since the heat conductivity of aluminum itself was high, there was a problem that sufficient heat insulation property was not obtained by heat conduction [a heat bridge] which lets a sheathing object pass. The approach [JP,8-159376,A] of using a stainless steel foil with comparatively small thermal conductivity etc. for the gas barrier layer of a sheathing object for the purpose of solution of this problem, the approach using the vacuum evaporationo film of aluminum, the ceramics, the approach [JP,7-113493,A and JP,8-152258,A] using the vacuum evaporationo film of glass, etc. are invented.
[0004] However, since the still in addition stainless heat conductivity is high, the approach using a stainless steel foil etc. of reduction of a heat bridge is inadequate. Moreover, although the approach using aluminum, the ceramics, or the vacuum evaporationo film of glass could be enough for reduction of a heat bridge, since a pinhole and a crack existed in the vacuum evaporationo film, gas barrier property was inadequate, and it was impossible to have continued at a long period of time and to have maintained the interior of a sheathing object at a vacua. It is offering the vacuum insulation material by which the gas barrier property of a sheathing object is [material] high, it continues at a long period of time, the vacua inside a sheathing object is maintained [this invention was made in view of such a situation, the place made into the purpose does not have migration of the heat which lets the sheathing object of vacuum insulation material pass, sufficient heat insulation property is obtained, and], and heat insulation property's is maintained.
[0005]
[The means for solving invention] In the vacuum insulation material which invention according to claim 1 enclosed heat insulation core material with the interior of the sheathing object which consists of a laminated film which has gas barrier property, and carried out evacuation of the interior of a sheathing object, it is the vacuum insulation material to which said laminated film is characterized by including the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material.
[0006] It is the vacuum insulation material according to claim 1 to which invention according to claim 2 is characterized by said organic substance film carrying out polymerization hardening of an electron ray or the ultraviolet-rays polymerization nature resin by the electron ray or ultraviolet rays.
[0007] Invention according to claim 3 is vacuum insulation material according to claim 1 or 2 to which thickness of said inorganic substance film is characterized by 5nm or more being 500nm or less.
[0008] In the vacuum insulation material which invention according to claim 4 enclosed heat insulation core material with the interior of the sheathing object which consists of a laminated film of two sheets which has gas barrier property, and carried out evacuation of the interior of a sheathing object, it is the vacuum insulation

material to which at least one in said laminated film is characterized by including the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material.
[0009] Invention according to claim 5 is vacuum insulation material given in either of claims 4 to which one sheet located in an elevated-temperature side among said laminated films is characterized by including the ingredient of thermal reflection.
[0010]
[Embodiment of the Invention] Hereafter, the gestalt of 1 operation of this invention is explained to a detail using drawing. The heat insulation core material 5 is enclosed with the interior of the sheathing object 1 containing the laminated film which has gas barrier property, evacuation of the interior of a sheathing object is carried out, and the vacuum insulation material of this invention is characterized by including the cascade screen of said laminated film, the organic substance film 7, and the inorganic substance film 8. the laminated films 2 and 3 with which the vacuum insulation material of this invention has gas barrier property — since — from the becoming sheathing object — becoming — the last — the method seal of four — carrying out — the laminated film 4 good also as vacuum insulation material which carries out (drawing 1) and has the gas barrier property of one sheet — since — it consists of a becoming sheathing object, and the method seal of three is carried out to the last, and good (drawing 2) also as vacuum insulation material.
[0011] The laminated film containing the cascade screen of the organic substance film of this invention and the inorganic substance film forms the cascade screen of the organic substance film and the inorganic substance film on a support base material at least. As a support base material, polyethylene terephthalate (PET), polyethylenenaphthalate (PEN), Polyester, such as polybutylene terephthalate (PBT), polyethylene (PE), Polyolefines, such as polypropylene (PP) and polystyrene (PS), Polyamides (PA), such as nylon 6 and Nylon 66, polyimide, Polyacrylate, a polyvinyl chloride (PVC), a polyvinylidene chloride (PVDC), It is no extending or the oriented film of polyvinyl alcohol (PVA), an ethylene-vinylalcohol copolymer (EVOH), a polycarbonate (PC), polyether sulfone (PES), polymethylmethacrylates (PMMA), etc. and these copolymers. In advance of formation of the cascade screen of the organic substance film and the inorganic substance film, the front face of these support base materials does not interfere, even if surface treatment, such as corona treatment, flame treatment, low-temperature plasma treatment, and a chemical treatment, is performed. Moreover, additives, such as an antistatic agent, an ultraviolet ray absorbent, a plasticizer, and lubricant, may be contained in these plastic film if needed.
[0012] As inorganic substance film in this invention, metal aluminum (aluminum), an aluminum oxide (AlO_x), Oxidation silicon (SiO_x), a magnesium oxide (MgO), a calcium oxide (CaO), Titanium oxide (TiO_2), a zirconium dioxide (ZrO_2), alumimium nitride (AlN), Titanium nitride (TiN), silicon nitride (Si_3N_4), acid alumimium nitride (AlO_xN_y), The independent film of inorganic substances, such as acid silicon nitride (SiO_xN_y), acid titanium nitride (TiO_xN_y), an indium stannic acid ghost (ITO), and indium cerium oxide (ICO), or the mixture film and cascade screen of two or more inorganic substances are used. Such inorganic substance film is formed of vacuum processes, such as a vacuum deposition method, the sputtering method, and chemical vapor deposition (CVD method). Moreover, although the thickness changes a little with classes of inorganic substance film, it is important that they are 5nm or more and 500nm or less. The inorganic substance prepared on the support base material as it is 5nm or less may become island shape, and may not become film-like, and when it is 500nm or more, it is because the film may break or it may separate from a support base material with own internal stress of film. Moreover, since a heat bridge may become large and heat insulation property may fall when the inorganic substance film is aluminum, it is important that it is especially 500nm or less. Moreover, if it is extent which checks neither gas barrier property ability nor heat insulation property, even if other components are contained in such inorganic substance film, it will not interfere.
[0013] If the organic substance film in this invention is prepared for the purpose of making smooth irregularity of a support base material front face, intercepting the crack of the inorganic substance film, and propagation of a defect, easing the internal stress in the inorganic substance film, protecting the inorganic substance film, etc. and accompanies these purposes, especially neither, such as the component, a presentation and thickness, and the formation approach, will be limited. However, since the speed of a polymerization cure rate and aging after coating are unnecessary, it is desirable to stiffen the resin of ultraviolet rays or electron ray polymerization nature with ultraviolet rays or an electron ray.
[0014] Specifically Isoamyl acrylate, laurylacrylate, stearylacrylate, Butoxy ethyl acrylate, ethoxy diethylene-glycol acrylate, Methoxy triethylene glycol acrylate, methoxy polyethylene-glycol acrylate, Methoxy dipropylene glycol acrylate, phenoxy ethyl acrylate, Phenoxy polyethylene-glycol acrylate, phenol EO denaturation acrylate, Nonyl phenol EO denaturation acrylate, tetrahydrofurfuryl acrylate, ISOBO nil acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropylacrylate, 2-AKURIRO yloxy ethyl succinic acid, 2-AKURIRO yloxy ethyl phthalic acid, a 2-AKURIRO yloxy ethyl-2-hydroxyethyl phthalic acid, Monofunctional

acrylate, such as 2-ethylhexyl carbitol acrylate and an N-vinyl-2-pyrrolidone, Methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, Isobutyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, n-lauryl methacrylate, alkyl methacrylate, tridecyl methacrylate, n-stearyl methacrylate, methoxy ethylene glycol methacrylate, Methoxy polyethylene-glycol methacrylate, cyclohexyl methacrylate, Tetrahydrofurfuryl methacrylate, benzyl methacrylate, Phenoxy ethyl methacrylate, ISOBO nil methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxy butyl methacrylate, Dimethylaminoethyl methacrylate, diethylamino ethyl methacrylate, A methacrylic acid, 2-METAKURIRO yloxy ethyl succinic acid, 2-meta-KURIRO yloxy ethylhexahydrophthalic acid, 2-meta-KURIRO yloxy ethyl-2-hydroxypropyl phthalate, Monofunctional methacrylate, such as glycidyl methacrylate, triethylene glycol diacrylate, Polyethylene-glycol diacrylate, neopentyl glycol diacrylate, 1.6-hexanediol diacrylate, 1.9-nonane diol diacrylate, Dimethylol tricyclodecane diacrylate, ethylene glycol dimethacrylate, Diethylene-glycol dimethacrylate, 1.4-butanediol dimethacrylate, 1.6-hexanedioldimethacrylate, 1.9-nonane diol dimethacrylate, Acrylate and methacrylate of two organic functions, such as glycerol dimethacrylate and 2-hydroxy-3-AKURIRO yloxy propyl methacrylate, Trimethylolpropane triacrylate, pentaerythritol thoria KURIRE-TO, Pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, Trimethylolpropanetrimethacrylate, pentaerythritol thoria KURIRE-TOHEKISA methylene di-isocyanate, Pentaerythritol thoria KURIRE-TOTORI range isocyanate, Pentaerythritol thoria KURIRE-TOISO holon diisocyanate, Dipentaerythritol hexaacrylate, a dipentaerythritol hexaacrylate caprolactone addition product, Although acrylate, methacrylate, etc. of three or more organic functions, such as a sorbitol hexa acrylate ethyleneoxide (EO) addition product, are mentioned, it is not limited to these.

[0015] Moreover, these acrylate and methacrylate may be used independently, and two or more may be mixed and used. Especially in the case of monofunctional acrylate or methacrylate, it mixes with the acrylate of two or more organic functions, or methacrylate, and is used. Moreover, an organic compound without other ultraviolet-rays hardenability and electron ray hardenability may be mixed, and you may use.

[0016] since such organic substance film carries out polymerization hardening by irradiating ultraviolet rays and an electron ray, it is possible also for the membrane formation in a vacuum whose membrane formation rate does not need after treatment, such as quick aging, and in-line-izing with the vacuum process for mixing of an impurity being avoided upwards and forming an inorganic substance is possible for it -- etc. -- it has the outstanding description. Moreover, although the thickness changes with the class of organic substance, the coating approaches, hardening means, etc., about 0.2-5.0 micrometers is suitable in general. When thinner than 0.2 micrometers, it is because the organic substance film may not turn into continuation film, and when thicker than 5.0 micrometers, it is because stress starts the inorganic substance film and the fall of barrier property may be seen by hardening contraction of the organic substance film.

[0017] After melting the desired organic substance and its mixture to a solvent and coating with approaches, such as gravure coating, as the membrane formation approach of such organic substance film, it is also one approach to volatilize a solvent in oven etc., to irradiate ultraviolet rays and an electron ray subsequently, and to carry out polymerization hardening. Moreover, it can be said that it is the approach for which it was most suitable from irradiating ultraviolet rays after making it condense as liquid membrane on the base material which the desired organic substance and its mixture were evaporated in the vacuum, and was cooled, and an electron ray, carrying out polymerization hardening, and moreover the organic substance film of the desired presentation of a flash evaporation method as the evaporation-in vacuum approach being easily obtained in this case at high speed.

[0018] Moreover, especially a limit may not be in the built-up sequence or the number of layers of said organic substance film and inorganic substance film, two or more organic substance film and inorganic substance film may be the same, and it may be another. Moreover, the laminating of the stratum functionale of further others is carried out besides the organic substance film and the inorganic substance film, and it is good also as a laminated film. For example, in order to thrust and to raise reinforcement, the laminating of the nylon etc. can be carried out.

[0019] The number of the laminated films which have said gas barrier property which carries out a sheathing object configuration in this invention may be two, and it is desirable that the laminated film by the side of an elevated temperature contains the ingredient of thermal reflection in that case, and it is desirable that the laminated film by the side of low temperature contains the cascade screen of said organic substance film and inorganic substance film. As a thermal reflex ingredient, a metallic foil etc. is mentioned, for example. If it does in this way, the heat from an elevated-temperature side is reflected and conduction of the heat by the side of low temperature can be reduced.

[0020] Furthermore, it comes to carry out the laminating of the sealant layer 9 to which laminated films 2, 3, and 4 become the outermost layer from the resin which has heat-sealing nature, such as polyethylene, polypropylene, and an ethylene copolymer. The laminating of such a sealant layer is carried out by laminating the

film-ized ingredient through adhesives (not shown), or extruding the fused resin directly.

[0021] Moreover, in order to use as vacuum insulation material of this invention, it is desirable as gas barrier property of said laminated films 2, 3, and 4 in oxygen transmittance and steam transmittance being 0.5 (cm3/m2, day) and below 0.1 (g/m2, day), respectively, and it is still more desirable in it being 0.1 (cm3/m2, day) and below 0.05 (g/m2, day).

[0022] The vacuum insulation material of this invention can be obtained by filling up with and vacuum-packing the adiathermic core material 4 by making into an inside the heat-sealing nature resin layer of a layered product which consists of such a configuration. The Plastic solid with which these adiathermic core materials fabricated powder, such as a silica, and a pearlite, a calcium silicate, in the fixed configuration is used.

[0023]

[Example] Next, one concrete example is given and the vacuum insulation material of this invention is explained in more detail.

[0024] The PET film [lumiler P60 Toray Industries make] with a <example 1> thickness of 12 micrometers was used as the base material 5, it coated with the acrylate monomer [triethylene glycol diacrylate] (henceforth, Ac1) so that the thickness after drying on the one side might be set to about 1 micrometer, and the organic substance film 7 was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. Then, after having used electron ray heating type rolling-up vacuum evaporationo equipment on this organic substance film 7, forming oxidation silicon (henceforth, SiOx) with a thickness of about 40nm and considering as the inorganic substance film 8, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on the inorganic substance film 8, it considered as the sealant layer 9, and the laminated film 4 of this invention was obtained. Subsequently, facing each other and the circumference were heat sealed for sealant layer 9 comrades of this laminated film, vacuum seal of the Plastic solid of a powder silica was carried out as heat insulation core material 5, and the vacuum insulation material shown in drawing 1 was obtained. The thermal conductivity measured in the gas barrier property [the oxygen transmission rate and the steam transmission rate] and this vacuum insulation material center section of the sheathing object of this vacuum insulation material was shown in Table 1.

[0025] Except having prepared the <example 2> organic substance film and the inorganic substance film like Ac1/SiOx/Ac1/SiOx/Ac1 sequentially from the base material side by the same thickness as an example 1, and the approach, it is the same approach as an example 1, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0026] The PET film [lumiler P60 Toray Industries make] with a <example 3> thickness of 12 micrometers was used as the base material 5, it coated with the acrylate monomer [tripropylene glycol diacrylate] (henceforth, Ac2) containing 5% of the weight of a photopolymerization initiator [the product made from IRGACURE 184 tiba SUPESHARUTI KEMIKARUZU] so that the thickness after drying on the one side might be set to about 1 micrometer, and the organic substance film 7 was formed by irradiating the ultraviolet rays of 120 mJ/cm2 and stiffening them. Then, after using electron ray heating type rolling-up vacuum evaporationo equipment as inorganic substance film 8 and forming metal aluminum (henceforth, aluminum) with a thickness of about 40nm on this organic substance film 7, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on the metal aluminum film, it considered as the sealant layer 9, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0027] Except having prepared the <example 4> organic substance film and the inorganic substance film like Ac2/aluminum/Ac2/aluminum/Ac2 sequentially from the base material side by the same thickness as an example 3, and the approach, it is the same approach as an example 3, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0028] The PET film [lumiler P60 Toray Industries make] with a <example 5> thickness of 12 micrometers was used as the base material 5, it coated with the acrylate monomer [pentaerythritol thoria KURIRE-TOHEKISA

methylene di-isocyanate] (henceforth, Ac3) so that the thickness after drying on the one side might be set to about 1 micrometer, and the organic substance film 7 was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. Then, after using the direct-current magnetron type rolling-up sputtering system as inorganic substance film 8 and forming an indium cerium oxide (henceforth, ICO) with a thickness of about 50nm on this organic substance film 7, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on this oxide film, it considered as the sealant layer 9, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0029] Except having prepared the <example 6> organic substance film and the inorganic substance film like Ac3/ICO/Ac3/ICO/Ac3 sequentially from the base material side by the same thickness as an example 5, and the approach, it is the same approach as an example 5, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0030] The PET film [lumiler P60 Toray Industries make] with a <example 7> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 3, the vacuum evaporationo layer of metal aluminum (aluminum) with a thickness of about 40nm was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the laminated film 2 by the side of an elevated temperature was obtained. Except having prepared the organic substance film and the inorganic substance film like Ac1/SiOx/Ac1/SiOx/Ac1 sequentially from the base material side by the same thickness as an example 1, and the approach By the same approach as an example 1, the vacuum insulation material which obtained the laminated film 3 by the side of the low temperature of this invention and which ranks second, heat seals facing each other and the circumference for sealant layer 9 comrades of these laminated films 2 and 3, carries out vacuum seal of the Plastic solid of a powder silica as heat insulation core material 5, and is shown in drawing 2 was obtained. The thermal conductivity measured in the gas barrier property [the oxygen transmission rate and the steam transmission rate] and this vacuum insulation material center section of the sheathing object of this vacuum insulation material was shown in Table 1.
[0031] The PET film [lumiler P60 Toray Industries make] with a <example 1 of comparison> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 1, the oxidation silicon layer (SiOx) with a thickness of about 40nm was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0032] The PET film [lumiler P60 Toray Industries make] with a <example 2 of comparison> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 3, the vacuum evaporationo layer of metal aluminum (aluminum) with a thickness of about 40nm was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0033] The PET film [lumiler P60 Toray Industries make] with a <example 3 of comparison> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 5, about 50nm indium cerium oxide layer (ICO) was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica

were measured like the example 1. The measurement result was shown in Table 1.

[0034] The PET film [lumiler P60 Toray Industries make] with a <example 4 of comparison> thickness of 12 micrometers was used as the base material, and it coated with the acrylate monomer [triethylene glycol diacrylate] (Ac1) so that the thickness after desiccation might be set to about 1 micrometer at the one side, and the polymer layer was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. The low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on the acrylate layer, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0035] The PET film [lumiler P60 Toray Industries make] with a <example 5 of comparison> thickness of 12 micrometers was used as the base material, and it coated with the acrylate monomer [tripropylene glycol diacrylate] (Ac2) containing 5% of the weight of a photopolymerization initiator [the product made from IRGACURE 184 tiba SUPESHARUTI KEMIKARUZU] so that the thickness after desiccation might be set to about 1 micrometer at the one side, and the polymer layer was formed by irradiating the ultraviolet rays of 120 mJ/cm2 and stiffening them. Then, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on this acrylate layer, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0036] The PET film [lumiler P60 Toray Industries make] with a <example 6 of comparison> thickness of 12 micrometers was used as the base material, and it coated with the acrylate monomer [pentaerythritol thoria KURIRE-TOHEKISA methylene di-isocyanate] (Ac3) so that the thickness after desiccation might be set to about 1 micrometer at the one side, and the polymer layer was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. Then, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on this acrylate layer, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0037] The PET film [lumiler P60 Toray Industries make] with a <example 7 of comparison> thickness of 12 micrometers was used as the base material, through polyester polyurethane system adhesives (not shown), metal aluminium foil with a thickness of 7 micrometers was laminated on that one side, it was followed, on this metal aluminium foil, the low consistency polyethylene film with a thickness of 60 micrometers was laminated using the same adhesives, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0038]

[Table 1]

	外装体中の[illegible]フィルムの 有[illegible]、無[illegible]の[illegible]	ガスバリア性 [illegible] (cm²/m²·day)	[illegible] (g/m²·day)	[illegible] (W/m·K)
[illegible]1	Ac1/SiOx	0.5	0.07	[illegible]
[illegible]2	Ac 1/SiOx/Ac 1/SiOx/Ac 1	0.03	0.02	[illegible]
[illegible]3	Ac 2/Al	0.05	0.05	[illegible]
[illegible]4	Ac 2/Al/Ac 2/Al/Ac 2	≦0.01	≦0.01	[illegible]
[illegible]5	Ac 3/ICO	≦0.01	≦0.01	[illegible]
[illegible]6	Ac 3/ICO/Ac 3/ICO/Ac 3	≦0.01	≦0.01	0.005
[illegible]7	[illegible]:Al [illegible]:Ac 1/SiOx/Ac 1/SiOx/Ac 1	0.5	0.8	0.005
比[illegible]1	SiOx	2.5	2	[illegible]
比[illegible]2	Al	0.5	[illegible]	[illegible]
比[illegible]3	ICO	2	2	[illegible]
比[illegible]4	Ac 1	140	52	[illegible]
比[illegible]5	Ac 2	140	[illegible]	[illegible]
比[illegible]6	Ac 3	140	[illegible]	[illegible]
比[illegible]7	Al[illegible]	[illegible]	[illegible]	[illegible]

[0039] As shown in examples 1-7, in order to continue at a long period of time and to maintain the interior of

vacuum insulation material at a high degree of vacuum by using the laminated film which has the gas barrier property containing the cascade screen of the organic substance film and the inorganic substance film on a support base material as a sheathing object of vacuum insulation material, the sheathing object which has indispensable high gas barrier property was acquired, and there is no heat conduction by the heat bridge, and the vacuum insulation material which has high heat insulation property was obtained. Moreover, although the result shown in the examples 1-3 of a comparison and the examples 4-6 of a comparison was a thing at the time of using only the inorganic substance film and the organic substance film as a laminated film, respectively, with these sheathing objects, the gas barrier property as a case of an example was not obtained. Since the organic substance film had hardly contributed to improvement in gas barrier property especially in the case of the examples 4-6 of a comparison, the degree of vacuum inside vacuum insulation material was low from the start, and early thermal conductivity was [/ else] also high. Moreover, although sufficient gas barrier property was obtained even if this sheathing object compared with the thing of an example, although the result shown in the example 7 of a comparison was a thing at the time of using metal aluminium foil as gas barrier property, in the vacuum insulation material using this sheathing object, high heat insulation property was not obtained by heat conduction by the heat bridge.

[0040]

[Effect of the Invention] In the vacuum insulation material to which heat insulation core material was enclosed with the sheathing inside of the body which consists of a laminated film which has gas barrier property according to this invention as stated above, and evacuation of the interior of a sheathing object was carried out When said laminated film contains the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material The gas barrier property of a sheathing object is high, it continues at a long period of time, the vacua inside a sheathing object is maintained [there is no migration of the heat which lets the sheathing object of vacuum insulation material pass sufficient heat insulation property is obtained, and], and the vacuum insulation material by which heat insulation property is maintained can be offered.

[0041]

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention is attached in a refrigerator, a low-temperature container, etc., and relates to the vacuum insulation material which demonstrates adiabatic efficiency.

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PRIOR ART

[Description of the Prior Art] Various heat insulators are used from the former, as a heat insulator which was excellent in heat insulation property especially, adiathermic core material is enclosed with the sheathing inside of the body, and the vacuum insulation material of a configuration of having carried out evacuation of the interior is used for the refrigerator or the low-temperature container. This sheathing object needs to be excellent in gas barrier property, in order to prevent invasion of the gas (air) from the outside and to hold the interior to a vacua for a long period of time. Then, in order to give high gas barrier property conventionally, the laminated film which contains metal aluminium foil with a thickness of about 7-15 micrometers as that of the gas barrier layer of a sheathing object has mainly been used.

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EFFECT OF THE INVENTION

[Effect of the Invention] In the vacuum insulation material to which heat insulation core material was enclosed with the sheathing inside of the body which consists of a laminated film which has gas barrier property according to this invention as stated above, and evacuation of the interior of a sheathing object was carried out When said laminated film contains the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material The gas barrier property of a sheathing object is high, it continues at a long period of time, the vacua inside a sheathing object is maintained [there is no migration of the heat which lets the sheathing object of vacuum insulation material pass sufficient heat insulation property is obtained, and], and the vacuum insulation material by which heat insulation property is maintained can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in the case of such aluminum foil, it excelled in gas barrier property, but since the heat conductivity of aluminum itself was high, there was a problem that sufficient heat insulation property was not obtained by heat conduction [a heat bridge] which lets a sheathing object pass. The approach [JP,8-159376,A] of using a stainless steel foil with comparatively small thermal conductivity etc. for the gas barrier layer of a sheathing object for the purpose of solution of this problem, the approach using the vacuum evaporationo film of aluminum, the ceramics, the approach [JP,7-113493,A and JP,8-152258,A] using the vacuum evaporationo film of glass, etc. are invented.
[0004] However, since the still in addition stainless heat conductivity is high, the approach using a stainless steel foil etc. of reduction of a heat bridge is inadequate. Moreover, although the approach using aluminum, the ceramics, or the vacuum evaporationo film of glass could be enough for reduction of a heat bridge, since a pinhole and a crack existed in the vacuum evaporationo film, gas barrier property was inadequate, and it was impossible to have continued at a long period of time and to have maintained the interior of a sheathing object at a vacua. It is offering the vacuum insulation material by which the gas barrier property of a sheathing object is [material] high, it continues at a long period of time, the vacua inside a sheathing object is maintained [this invention was made in view of such a situation, the place made into the purpose does not have migration of the heat which lets the sheathing object of vacuum insulation material pass, sufficient heat insulation property is obtained, and], and heat insulation property's is maintained.

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MEANS

[The means for solving invention] In the vacuum insulation material which invention according to claim 1 enclosed heat insulation core material with the interior of the sheathing object which consists of a laminated film which has gas barrier property, and carried out evacuation of the interior of a sheathing object, it is the vacuum insulation material to which said laminated film is characterized by including the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material.
[0006] It is the vacuum insulation material according to claim 1 to which invention according to claim 2 is characterized by said organic substance film carrying out polymerization hardening of an electron ray or the ultraviolet-rays polymerization nature resin by the electron ray or ultraviolet rays.
[0007] Invention according to claim 3 is vacuum insulation material according to claim 1 or 2 to which thickness of said inorganic substance film is characterized by 5nm or more being 500nm or less.
[0008] In the vacuum insulation material which invention according to claim 4 enclosed heat insulation core material with the interior of the sheathing object which consists of a laminated film of two sheets which has gas barrier property, and carried out evacuation of the interior of a sheathing object, it is the vacuum insulation material to which at least one in said laminated film is characterized by including the cascade screen of the organic substance film and inorganic substance film which were formed on the support base material.
[0009] Invention according to claim 5 is vacuum insulation material given in either of claims 4 to which one sheet located in an elevated-temperature side among said laminated films is characterized by including the ingredient of thermal reflection.
[0010]
[Embodiment of the Invention] Hereafter, the gestalt of 1 operation of this invention is explained to a detail using drawing. The heat insulation core material 5 is enclosed with the interior of the sheathing object 1 containing the laminated film which has gas barrier property, evacuation of the interior of a sheathing object is carried out, and the vacuum insulation material of this invention is characterized by including the cascade screen of said laminated film, the organic substance film 7, and the inorganic substance film 8. the laminated films 2 and 3 with which the vacuum insulation material of this invention has gas barrier property — since — from the becoming sheathing object — becoming — the last — the method seal of four — carrying out — the laminated film 4 good also as vacuum insulation material which carries out (drawing 1) and has the gas barrier property of one sheet — since — it consists of a becoming sheathing object, and the method seal of three is carried out to the last, and good (drawing 2) also as vacuum insulation material.
[0011] The laminated film containing the cascade screen of the organic substance film of this invention and the inorganic substance film forms the cascade screen of the organic substance film and the inorganic substance film on a support base material at least. As a support base material, polyethylene terephthalate (PET), polyethylenenaphthalate (PEN), Polyester, such as polybutylene terephthalate (PBT), polyethylene (PE), Polyolefines, such as polypropylene (PP) and polystyrene (PS), Polyamides (PA), such as nylon 6 and Nylon 66, polyimide, Polyacrylate, a polyvinyl chloride (PVC), a polyvinylidene chloride (PVDC), It is no extending or the oriented film of polyvinyl alcohol (PVA), an ethylene-vinylalcohol copolymer (EVOH), a polycarbonate (PC), polyether sulfone (PES), polymethylmethacrylates (PMMA), etc. and these copolymers. In advance of formation of the cascade screen of the organic substance film and the inorganic substance film, the front face of these support base materials does not interfere, even if surface treatment, such as corona treatment, flame treatment, low-temperature plasma treatment, and a chemical treatment, is performed. Moreover, additives, such as an antistatic agent, an ultraviolet ray absorbent, a plasticizer, and lubricant, may be contained in these plastic film if needed.
[0012] As inorganic substance film in this invention, metal aluminum (aluminum), an aluminum oxide (AlOx), Oxidation silicon (SiOx), a magnesium oxide (MgO), a calcium oxide (CaO), Titanium oxide (TiO_2), a zirconium dioxide (ZrO_2), alumimium nitride (AlN), Titanium nitride (TiN), silicon nitride (Si_3N_4), acid alumimium nitride

(AlOxNy), The independent film of inorganic substances, such as acid silicon nitride (SiOxNy), acid titanium nitride (TiOxNy), an indium stannic acid ghost (ITO), and indium cerium oxide (ICO), or the mixture film and cascade screen of two or more inorganic substances are used. Such inorganic substance film is formed of vacuum processes, such as a vacuum deposition method, the sputtering method, and chemical vapor deposition (CVD method). Moreover, although the thickness changes a little with classes of inorganic substance film, it is important that they are 5nm or more and 500nm or less. The inorganic substance prepared on the support base material as it is 5nm or less may become island shape, and may not become film-like, and when it is 500nm or more, it is because the film may break or it may separate from a support base material with own internal stress of film. Moreover, since a heat bridge may become large and heat insulation property may fall when the inorganic substance film is aluminum, it is important that it is especially 500nm or less. Moreover, if it is extent which checks neither gas barrier property ability nor heat insulation property, even if other components are contained in such inorganic substance film, it will not interfere.

[0013] If the organic substance film in this invention is prepared for the purpose of making smooth irregularity of a support base material front face, intercepting the crack of the inorganic substance film, and propagation of a defect, easing the internal stress in the inorganic substance film, protecting the inorganic substance film, etc. and accompanies these purposes, especially neither, such as the component, a presentation and thickness, and the formation approach, will be limited. However, since the speed of a polymerization cure rate and aging after coating are unnecessary, it is desirable to stiffen the resin of ultraviolet rays or electron ray polymerization nature with ultraviolet rays or an electron ray.

[0014] Specifically Isoamyl acrylate, laurylacrylate, stearylacrylate, Butoxy ethyl acrylate, ethoxy diethylene-glycol acrylate, Methoxy triethylene glycol acrylate, methoxy polyethylene-glycol acrylate, Methoxy dipropylene glycol acrylate, phenoxy ethyl acrylate, Phenoxy polyethylene-glycol acrylate, phenol EO denaturation acrylate, Nonyl phenol EO denaturation acrylate, tetrahydrofurfuryl acrylate, ISOBO nil acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropylacrylate, 2-AKURIRO yloxy ethyl succinic acid, 2-AKURIRO yloxy ethyl phthalic acid, a 2-AKURIRO yloxy ethyl-2-hydroxyethyl phthalic acid, Monofunctional acrylate, such as 2-ethylhexyl carbitol acrylate and an N-vinyl-2-pyrrolidone, Methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, Isobutyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, n-lauryl methacrylate, alkyl methacrylate, tridecyl methacrylate, n-stearyl methacrylate, methoxy ethylene glycol methacrylate, Methoxy polyethylene-glycol methacrylate, cyclohexyl methacrylate, Tetrahydrofurfuryl methacrylate, benzyl methacrylate, Phenoxy ethyl methacrylate, ISOBO nil methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxy butyl methacrylate, Dimethylaminoethyl methacrylate, diethylamino ethyl methacrylate, A methacrylic acid, 2-METAKURIRO yloxy ethyl succinic acid, 2-meta-KURIRO yloxy ethylhexahydrophthalic acid, 2-meta-KURIRO yloxy ethyl-2-hydroxypropyl phthalate, Monofunctional methacrylate, such as glycidyl methacrylate, triethylene glycol diacrylate, Polyethylene-glycol diacrylate, neopentyl glycol diacrylate, 1.6-hexanediol diacrylate, 1.9-nonane diol diacrylate, Dimethylol tricyclodecane diacrylate, ethylene glycol dimethacrylate, Diethylene-glycol dimethacrylate, 1.4-butanediol dimethacrylate, 1.6-hexanedioldimethacrylate, 1.9-nonane diol dimethacrylate, Acrylate and methacrylate of two organic functions, such as glycerol dimethacrylate and 2-hydroxy-3-AKURIRO yloxy propyl methacrylate, Trimethylolpropane triacrylate, pentaerythritol thoria KURIRE-TO, Pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, Trimethylolpropanetrimethacrylate, pentaerythritol thoria KURIRE-TOHEKISA methylene di-isocyanate, Pentaerythritol thoria KURIRE-TOTORI range isocyanate, Pentaerythritol thoria KURIRE-TOISO holon diisocyanate, Dipentaerythritol hexaacrylate, a dipentaerythritol hexaacrylate caprolactone addition product, Although acrylate, methacrylate, etc. of three or more organic functions, such as a sorbitol hexa acrylate ethyleneoxide (EO) addition product, are mentioned, it is not limited to these.

[0015] Moreover, these acrylate and methacrylate may be used independently, and two or more may be mixed and used. Especially in the case of monofunctional acrylate or methacrylate, it mixes with the acrylate of two or more organic functions, or methacrylate, and is used. Moreover, an organic compound without other ultraviolet-rays hardenability and electron ray hardenability may be mixed, and you may use.

[0016] since such organic substance film carries out polymerization hardening by irradiating ultraviolet rays and an electron ray, it is possible also for the membrane formation in a vacuum whose membrane formation rate does not need after treatment, such as quick aging, and in-line-izing with the vacuum process for mixing of an impurity being avoided upwards and forming an inorganic substance is possible for it — etc. — it has the outstanding description. Moreover, although the thickness changes with the class of organic substance, the coating approaches, hardening means, etc., about 0.2-5.0 micrometers is suitable in general. When thinner than 0.2 micrometers, it is because the organic substance film may not turn into continuation film, and when thicker than 5.0 micrometers, it is because stress starts the inorganic substance film and the fall of barrier property may be seen by hardening contraction of the organic substance film.

[0017] After melting the desired organic substance and its mixture to a solvent and coating with approaches, such as gravure coating, as the membrane formation approach of such organic substance film, it is also one approach to volatilize a solvent in oven etc., to irradiate ultraviolet rays and an electron ray subsequently, and to carry out polymerization hardening. Moreover, it can be said that it is the approach for which it was most suitable from irradiating ultraviolet rays after making it condense as liquid membrane on the base material which the desired organic substance and its mixture were evaporated in the vacuum, and was cooled, and an electron ray, carrying out polymerization hardening, and moreover the organic substance film of the desired presentation of a flash evaporation method as the evaporation-in vacuum approach being easily obtained in this case at high speed.

[0018] Moreover, especially a limit may not be in the built-up sequence or the number of layers of said organic substance film and inorganic substance film, two or more organic substance film and inorganic substance film may be the same, and it may be another. Moreover, the laminating of the stratum functionale of further others is carried out besides the organic substance film and the inorganic substance film, and it is good also as a laminated film. For example, in order to thrust and to raise reinforcement, the laminating of the nylon etc. can be carried out.

[0019] The number of the laminated films which have said gas barrier property which carries out a sheathing object configuration in this invention may be two, and it is desirable that the laminated film by the side of an elevated temperature contains the ingredient of thermal reflection in that case, and it is desirable that the laminated film by the side of low temperature contains the cascade screen of said organic substance film and inorganic substance film. As a thermal reflex ingredient, a metallic foil etc. is mentioned, for example. If it does in this way, the heat from an elevated-temperature side is reflected and conduction of the heat by the side of low temperature can be reduced.

[0020] Furthermore, it comes to carry out the laminating of the sealant layer 9 to which laminated films 2, 3, and 4 become the outermost layer from the resin which has heat-sealing nature, such as polyethylene, polypropylene, and an ethylene copolymer. The laminating of such a sealant layer is carried out by laminating the film-ized ingredient through adhesives (not shown), or extruding the fused resin directly.

[0021] Moreover, in order to use as vacuum insulation material of this invention, it is desirable as gas barrier property of said laminated films 2, 3, and 4 in oxygen transmittance and steam transmittance being 0.5 (cm3/m2, day) and below 0.1 (g/m2, day), respectively, and it is still more desirable in it being 0.1 (cm3/m2, day) and below 0.05 (g/m2, day).

[0022] The vacuum insulation material of this invention can be obtained by filling up with and vacuum-packing the adiathermic core material 4 by making into an inside the heat-sealing nature resin layer of a layered product which consists of such a configuration. The Plastic solid with which these adiathermic core materials fabricated powder, such as a silica, and a pearlite, a calcium silicate, in the fixed configuration is used.

[Translation done.]

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EXAMPLE

[Example] Next, one concrete example is given and the vacuum insulation material of this invention is explained in more detail.
[0024] The PET film [lumiler P60 Toray Industries make] with a <example 1> thickness of 12 micrometers was used as the base material 5, it coated with the acrylate monomer [triethylene glycol diacrylate] (henceforth, Ac1) so that the thickness after drying on the one side might be set to about 1 micrometer, and the organic substance film 7 was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. Then, after having used electron ray heating type rolling-up vacuum evaporationo equipment on this organic substance film 7, forming oxidation silicon (henceforth, SiOx) with a thickness of about 40nm and considering as the inorganic substance film 8, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on the inorganic substance film 8, it considered as the sealant layer 9, and the laminated film 4 of this invention was obtained. Subsequently, facing each other and the circumference were heat sealed for sealant layer 9 comrades of this laminated film, vacuum seal of the Plastic solid of a powder silica was carried out as heat insulation core material 5, and the vacuum insulation material shown in drawing 1 was obtained. The thermal conductivity measured in the gas barrier property [the oxygen transmission rate and the steam transmission rate] and this vacuum insulation material center section of the sheathing object of this vacuum insulation material was shown in Table 1.
[0025] Except having prepared the <example 2> organic substance film and the inorganic substance film like Ac1/SiOx/Ac1/SiOx/Ac1 sequentially from the base material side by the same thickness as an example 1, and the approach, it is the same approach as an example 1, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0026] The PET film [lumiler P60 Toray Industries make] with a <example 3> thickness of 12 micrometers was used as the base material 5, it coated with the acrylate monomer [tripropylene glycol diacrylate] (henceforth, Ac2) containing 5% of the weight of a photopolymerization initiator [the product made from IRGACURE 184 tiba SUPESHARUTI KEMIKARUZU] so that the thickness after drying on the one side might be set to about 1 micrometer, and the organic substance film 7 was formed by irradiating the ultraviolet rays of 120 mJ/cm2 and stiffening them. Then, after using electron ray heating type rolling-up vacuum evaporationo equipment as inorganic substance film 8 and forming metal aluminum (henceforth, aluminum) with a thickness of about 40nm on this organic substance film 7, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on the metal aluminum film, it considered as the sealant layer 9, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0027] Except having prepared the <example 4> organic substance film and the inorganic substance film like Ac2/aluminum/Ac2/aluminum/Ac2 sequentially from the base material side by the same thickness as an example 3, and the approach, it is the same approach as an example 3, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0028] The PET film [lumiler P60 Toray Industries make] with a <example 5> thickness of 12 micrometers was used as the base material 5, it coated with the acrylate monomer [pentaerythritol thoria KURIRE-TOHEKISA methylene di-isocyanate] (henceforth, Ac3) so that the thickness after drying on the one side might be set to about 1 micrometer, and the organic substance film 7 was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. Then, after using the direct-current magnetron type rolling-up sputtering system as inorganic substance film 8 and forming an indium cerium oxide (henceforth, ICO) with a thickness of about 50nm on this organic substance film 7, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on this oxide film, it considered as the sealant layer 9, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0029] Except having prepared the <example 6> organic substance film and the inorganic substance film like Ac3/ICO/Ac3/ICO/Ac3 sequentially from the base material side by the same thickness as an example 5, and the approach, it is the same approach as an example 5, and the laminated film 4 of this invention was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this laminated film, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0030] The PET film [lumiler P60 Toray Industries make] with a <example 7> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 3, the vacuum evaporationo layer of metal aluminum (aluminum) with a thickness of about 40nm was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the laminated film 2 by the side of an elevated temperature was obtained. Except having prepared the organic substance film and the inorganic substance film like Ac1/SiOx/Ac1/SiOx/Ac1 sequentially from the base material side by the same thickness as an example 1, and the approach By the same approach as an example 1, the vacuum insulation material which obtained the laminated film 3 by the side of the low temperature of this invention and which ranks second, heat seals facing each other and the circumference for sealant layer 9 comrades of these laminated films 2 and 3, carries out vacuum seal of the Plastic solid of a powder silica as heat insulation core material 5, and is shown in drawing 2 was obtained. The thermal conductivity measured in the gas barrier property [the oxygen transmission rate and the steam transmission rate] and this vacuum insulation material center section of the sheathing object of this vacuum insulation material was shown in Table 1.
[0031] The PET film [lumiler P60 Toray Industries make] with a <example 1 of comparison> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 1, the oxidation silicon layer (SiOx) with a thickness of about 40nm was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0032] The PET film [lumiler P60 Toray Industries make] with a <example 2 of comparison> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 3, the vacuum evaporationo layer of metal aluminum (aluminum) with a thickness of about 40nm was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.
[0033] The PET film [lumiler P60 Toray Industries make] with a <example 3 of comparison> thickness of 12 micrometers was used as the base material, on the one side, by the same approach as an example 5, about 50nm indium cerium oxide layer (ICO) was prepared, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on it, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat

sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0034] The PET film [lumiler P60 Toray Industries make] with a <example 4 of comparison> thickness of 12 micrometers was used as the base material, and it coated with the acrylate monomer [triethylene glycol diacrylate] (Ac1) so that the thickness after desiccation might be set to about 1 micrometer at the one side, and the polymer layer was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. The low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on the acrylate layer, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0035] The PET film [lumiler P60 Toray Industries make] with a <example 5 of comparison> thickness of 12 micrometers was used as the base material, and it coated with the acrylate monomer [tripropylene glycol diacrylate] (Ac2) containing 5% of the weight of a photopolymerization initiator [the product made from IRGACURE 184 tiba SUPESHARUTI KEMIKARUZU] so that the thickness after desiccation might be set to about 1 micrometer at the one side, and the polymer layer was formed by irradiating the ultraviolet rays of 120 mJ/cm2 and stiffening them. Then, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on this acrylate layer, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0036] The PET film [lumiler P60 Toray Industries make] with a <example 6 of comparison> thickness of 12 micrometers was used as the base material, and it coated with the acrylate monomer [pentaerythritol thoria KURIRE-TOHEKISA methylene di-isocyanate] (Ac3) so that the thickness after desiccation might be set to about 1 micrometer at the one side, and the polymer layer was formed by irradiating the electron ray of the acceleration voltage of 120kV, and quantity-of-radiation 10Mrad, and stiffening it. Then, the low consistency polyethylene film with a thickness of 60 micrometers was laminated through polyester polyurethane system adhesives (not shown) on this acrylate layer, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0037] The PET film [lumiler P60 Toray Industries make] with a <example 7 of comparison> thickness of 12 micrometers was used as the base material, through polyester polyurethane system adhesives (not shown), metal aluminium foil with a thickness of 7 micrometers was laminated on that one side, it was followed, on this metal aluminium foil, the low consistency polyethylene film with a thickness of 60 micrometers was laminated using the same adhesives, it considered as the sealant layer, and the layered product was obtained. Facing each other and the circumference were heat sealed for the sealant layers of this layered product, and the gas barrier property and the thermal conductivity of the vacuum insulation material which carried out vacuum seal and acquired the Plastic solid of a powder silica were measured like the example 1. The measurement result was shown in Table 1.

[0038]

[Table 1]

	外装体中の積層フィルムの有機物層、無機物層の層構成	ガスバリア性 酸素 (cm³/m²·day)	ガスバリア性 水蒸気 (g/m²·day)	熱伝導率 (W/m·K)
実施例1	Ac1／SiOx	0.5	0.07	[illegible]
実施例2	Ac 1／SiOx／Ac 1／SiOx／Ac 1	0.02	0.02	[illegible]
実施例3	Ac 2／Al	0.05	0.05	[illegible]
実施例4	Ac 2／Al／Ac 2／Al／Ac 2	≦0.01	≦0.01	[illegible]
実施例5	Ac 3／ICO	≦0.01	≦0.01	[illegible]
実施例6	Ac 3／ICO／Ac 3／ICO／Ac 3	≦0.01	≦0.01	[illegible]
実施例7	[illegible]:Al [illegible]:Ac 1／SiOx／Ac 1／SiOx／Ac 1	0.5	0.8	0.005
比較例1	SiOx	2.5	2	[illegible]
比較例2	Al	0.5	0.8	0.030
比較例3	ICO	2	2	[illegible]
比較例4	Ac 1	140	82	[illegible]
比較例5	Ac 2	140	82	[illegible]
比較例6	Ac 3	140	[illegible]	[illegible]
比較例7	Al箔	[illegible]	[illegible]	[illegible]

[0039] As shown in examples 1-7, in order to continue at a long period of time and to maintain the interior of vacuum insulation material at a high degree of vacuum by using the laminated film which has the gas barrier property containing the cascade screen of the organic substance film and the inorganic substance film on a support base material as a sheathing object of vacuum insulation material, the sheathing object which has indispensable high gas barrier property was acquired, and there is no heat conduction by the heat bridge, and the vacuum insulation material which has high heat insulation property was obtained. Moreover, although the result shown in the examples 1-3 of a comparison and the examples 4-6 of a comparison was a thing at the time of using only the inorganic substance film and the organic substance film as a laminated film, respectively, with these sheathing objects, the gas barrier property as a case of an example was not obtained. Since the organic substance film had hardly contributed to improvement in gas barrier property especially in the case of the examples 4-6 of a comparison, the degree of vacuum inside vacuum insulation material was low from the start, and early thermal conductivity was [/ else] also high. Moreover, although sufficient gas barrier property was obtained even if this sheathing object compared with the thing of an example, although the result shown in the example 7 of a comparison was a thing at the time of using metal aluminium foil as gas barrier property, in the vacuum insulation material using this sheathing object, high heat insulation property was not obtained by heat conduction by the heat bridge.

[Translation done.]

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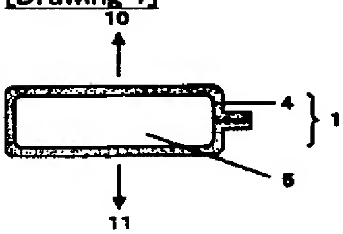
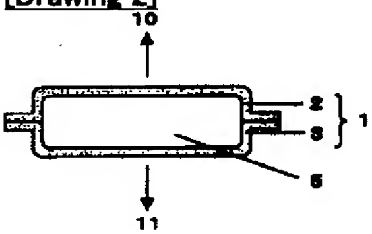
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

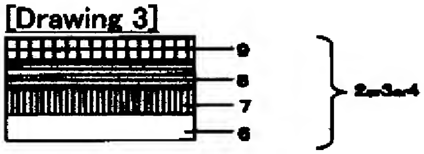
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]